

ORGANIC CHEMICAL BULLETIN

Volume 21 • 1949 • Number 2

PUBLISHED BY

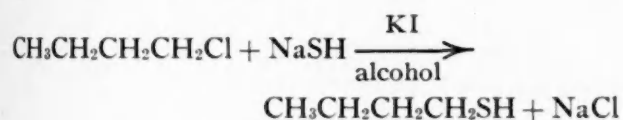
the Research Laboratories

*of the Eastman Kodak Company,
Rochester 4, N. Y.*

Mercaptans

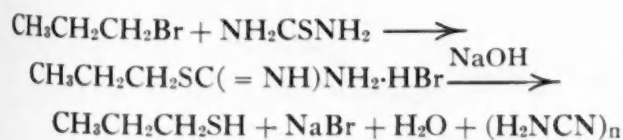
By DANA L. FRENCH*

A direct approach in the synthesis of mercaptans is the substitution of an inorganic radical already present in an organic compound by an SH group from an inorganic source, such as hydrogen sulfide, a sulfide, or a hydrosulfide. Thus, mercaptans are prepared in 75 to 85 per cent yields by the reaction of alkyl halides with an alcoholic solution of sodium or potassium hydrosulfide. The reaction of some of the alkyl chlorides with a hydrosulfide is facilitated by the use of potassium iodide as a catalyst.



Other alkylating agents behave similarly; sodium ethyl sulfate was the alkylating agent in the first synthesis of a mercaptan reported in the literature (1).

Alkyl halides and alkyl sulfates react readily with thiourea. The products are isothiuronium salts. An addition of alkali liberates the free isothiurea; however, these salts are not stable and decompose to yield mercaptans (80 to 90 per cent) and polymers.

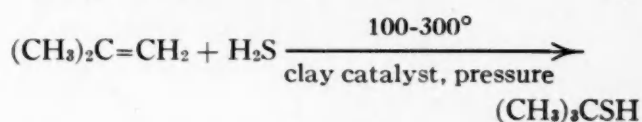


The alkyl chlorides react slowly and require a longer reflux period than the

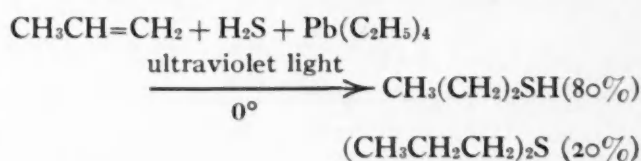
bromides and iodides. Isothiuronium salts may also be prepared directly from an alcohol, dry hydrogen chloride, and thiourea (2). This procedure may be applied with success to hexyl, octyl, and other higher aliphatic alcohols.

H₂S-Olefin Reaction

Hydrogen sulfide and olefins react to form mercaptans in either the "normal" or "abnormal" manner with reference to Markownikoff's rule. The normal addition does not occur readily and requires high pressures and temperatures.



The abnormal addition does occur readily by a photochemical process (3). The addition takes place in the presence of metallohydrocarbon compounds and under the influence of ultraviolet radiation of a wave length below 3000 Å. The metallohydrocarbon compounds may include metal alkyls and aryls of lead, mercury, and tin. Thus, propylene and butylene are converted to the primary mercaptans in yields of 80 to 95 per cent respectively.

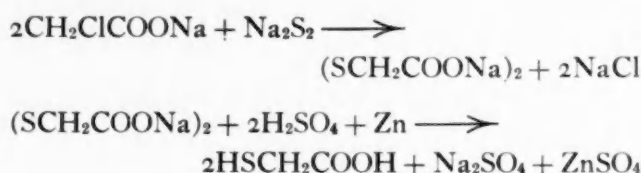


Of the series of primary mercaptans, the lowest two, methyl mercaptan and

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ethyl mercaptan, are readily volatile and may be used as stabilizers for adhesives of the polyvinyl type.

The formation of mercaptans by a cleavage of disulfides with potassium sulfide, zinc and acid, or metallic sodium is of limited usefulness since the disulfides are generally no more readily available than the mercaptans. But in specific cases, this procedure is valuable in forming the necessary sulfhydryl group. For example, thioglycolic acid may be formed in yields of about 65 per cent by the zinc and acid reduction of sodium dithiodiglycolate.

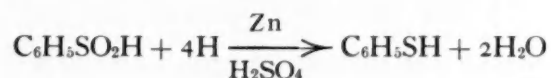
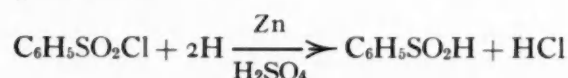


Arylthiols

Arylthiols may be produced by hydrogenation of sulfonic acids, sulfinic acids, their thio analogs, and compounds hydrolyzable to these acids. Thiophenol is obtained in yields of 87 per cent when benzenesulfinic acid is hydrogenated in 1,4-dioxane with sulfur and cobalt polysulfide catalyst. When using pyrophoric iron in place of the cobalt polysulfide, *p*-thiocresol is obtained in 84 per cent yields (4).

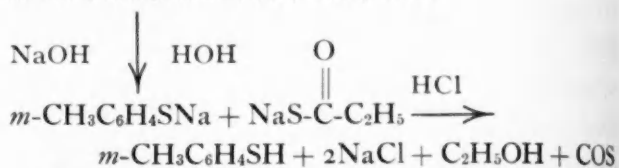
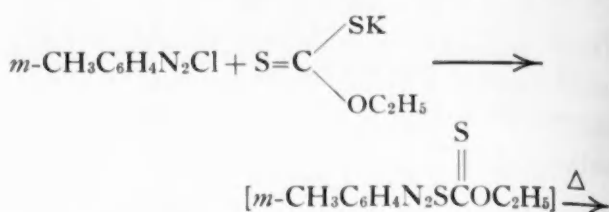
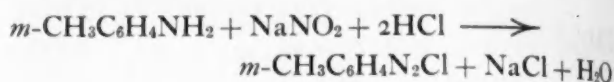
The *para*-substituted thiophenols may also be prepared by the reduction of the aromatic sulfonylchlorides with zinc and aqueous acid or with stannous chloride.

The yield for thiophenol is generally above 90 per cent and for *p*-thiocresol, 80 per cent.



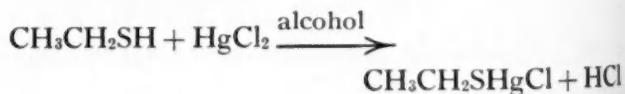
The *meta*- and *ortho*-thiocresols may be prepared from the diazonium salt. Cold solutions of the diazonium salt of *meta*- or *ortho*-toluidine and potassium ethyl xanthate produce a diazonium

xanthate which, upon warming, forms the S-aryl ethyl xanthate. An alkaline hydrolysis yields the respective thio-cresol; for example, *m*-thiocresol may be obtained in 70 per cent yields.

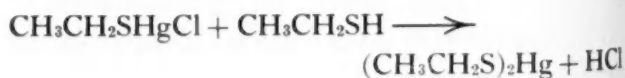


The use of aryl mercaptans as intermediates in the synthesis of dyes has been of great importance, particularly vat dyes. Thus, aminothiophenol serves as the starting point for indamine colors and thio acids as the intermediates for the thioindigo dyes. Specific examples of uses for aryl mercaptans occur in the rubber industry. Mercaptobenzothiazole, prepared in large quantities by the action of aniline and carbon disulfide, is used as an accelerator in vulcanizing.

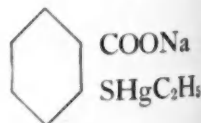
The name "mercaptans" results from the ready reaction of this series of compounds of the general formula RSH with mercury salts. Alkylmercaptomercuric chlorides, for example, may be obtained from the reaction of mercaptans with mercuric chloride in alcohol.



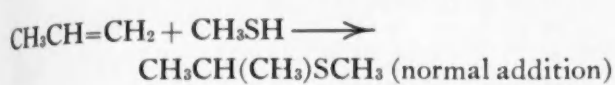
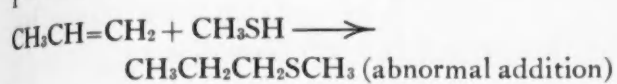
Further reaction with mercaptan yields a highly insoluble mercaptide.



An unsymmetrical mercury mercaptide, "merthiolate," may be used as a germicide.



The addition of mercaptans to unsaturated compounds yields either of two products.

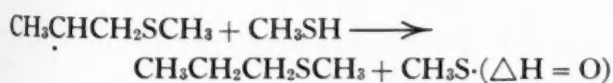
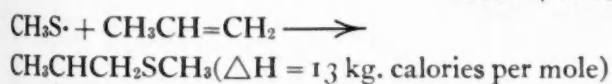
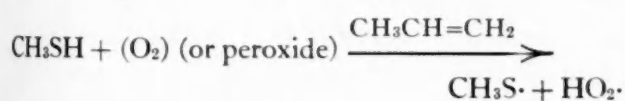


These two possible reactions are designated "normal" and "abnormal" additions on the assumption that mercaptans add normally as halogen acids.

Alkene Addition Catalysts

The abnormal addition of mercaptans to olefins and alkenes is catalyzed by oxygen and peroxides. Other catalysts or sensitizers include aliphatic and aromatic ketones, aldehydes, and acid halides. The latter are used as catalysts in a photochemical process effecting the addition of mercaptans to symmetrical or unsymmetrical unsaturated aliphatic hydrocarbons. The addition takes place in the presence of metallohydrocarbon compounds and under the influence of an ultraviolet light capable of photochemically dissociating these catalysts (3).

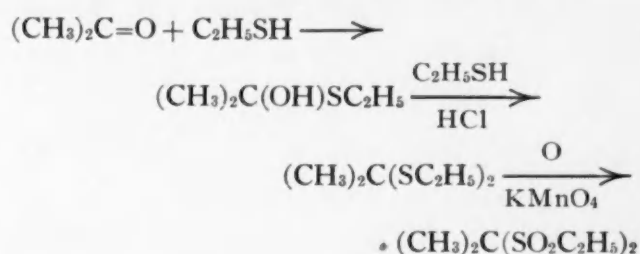
A definite proposal has been made showing that the abnormal addition takes place through a chain reaction involving free radicals (5).



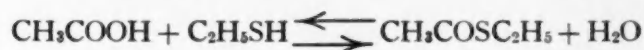
Normal addition of mercaptans to alkenes takes place when sulfur and iron sulfide are used as catalysts. When an alkene is exposed to air, the peroxides formed are sufficient to catalyze the abnormal addition. A careful purification of these reactants and exclusion of air prevent, or greatly retard, any abnormal addition (6).

Condensations with aldehydes, ketones, ketonic acids, and sugars may

take place with mercaptans. Sulfonal, one of the disulfones, may be made by the oxidation of the dimercaptol formed from acetone and ethyl mercaptan.

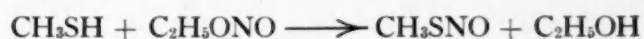


Esterifications are accomplished directly in many cases with mercaptans and carboxylic acids (other than formic acid). The reaction is analogous to the esterification of alcohols.



It is a reversible reaction and the equilibrium is unfavorable for the formation of thioesters in good yields.

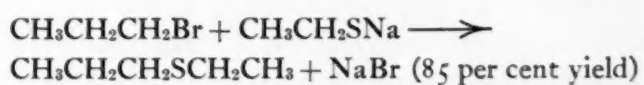
An ester exchange takes place when mercaptans react with organic nitrites to give a thionitrite and an alcohol or a phenol.



Occasionally an esterification fails, as for example, that of allyl mercaptan with formic acid, but this may be caused by the instability of the mercaptan.

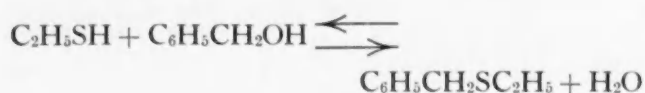
Compounds of the general formula $\text{RR}'\text{CR}''\text{SX}$ (in which R is a saturated hydrocarbon radical, R' and R'' are hydrocarbon radicals, and X is an ester group) are useful as corrosion inhibitors and froth-flotation agents. Thioesters are also useful in some applications as solvents and plasticizers.

The formation of sulfides from organic halides and sodium mercaptides is a reaction related to the Williamson synthesis.

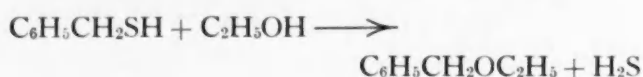


The reactions are not limited to sodium mercaptides. A frequent variant is found in the use of sodium ethoxide with the mercaptan and halogen derivative.

A sulfide may be formed by the action of some mercaptans with an alcohol.



Apparently this is not always the case, for benzyl mercaptan reacts irreversibly with ethyl alcohol to form the ether.



The first step in the oxidation of mercaptans is the formation of disulfides, and the last step is sulfonic acid formation. The sulfoxides and sulfones exist as intermediates. For the preparation of disulfides, it is necessary to select an oxidizing agent which will not oxidize disulfides. Convenient laboratory methods involve the reaction of a mercaptan compound in aqueous alkali with iodine or hydrogen peroxide, and yields of about 80 per cent are obtained.



Ferric chloride, lead peroxide, copper sulfate, phosphorous oxychloride, tellurium tetrachloride, and ferricyanides

may serve the same purpose. Air alone is quite adequate in production of disulfides from mercaptans. In fact, it is difficult to keep solution of mercaptans in oil from oxidizing. This is particularly marked under alkaline conditions.

A careful distinction must be made when mercaptans are oxidized by halogens. Iodine seems to be the only one that yields disulfides under alkaline conditions. Under acid conditions bromine and chlorine yield sulfobromides and sulfochlorides, but when alkaline conditions are maintained they lead to sulfoxides, sulfones, and sulfonic acid.

References

- (1) Zeise, *Ann.*, **11**, 1 (1834); Liebig, *Ann.*, **11**, 14 (1834)
- (2) Johnson and Sprague, *J. A. C. S.*, **58**, 1348 (1936)
- (3) Evans, Vaughn, and Rust, U. S. Patent 2,411,961.
- (4) Lazier and Signaigo, U. S. Patent 2,402,641.
- (5) Kharasch, Read, and Mayo, *Chem. and Ind.*, **57**, 754 (1938).
- (6) Jones and Reid, *J. A. C. S.*, **60**, 2452 (1938).

New Eastman Organic Chemicals

P 6119	Butane-1,2,3,4-tetracarboxylic Acid (Pract.)		
	MP 185° dec.....	100 g.	\$ 4.00 C
	HOCOCH ₂ (CHCOOH) ₂ CH ₂ COOH...MW 234.16		
P 6108	Di-n-butyltin Diacetate (Pract.) BP 138-139°/5 mm.	100 g.	2.00 C
	[CH ₃ (CH ₂) ₃] ₂ Sn(OCOCH ₃) ₂ ...MW 351.01		
P 6107	Di-n-butyltin Dichloride (Pract.) MP 39-41°	100 g.	2.00 C
	[CH ₃ (CH ₂) ₃] ₂ SnCl ₂ ...MW 303.84		
P 5197	2,6-Dichlorobenzaldehyde (Pract.) MP 69-72°	100 g.	6.00 C
	Cl ₂ C ₆ H ₃ CHO...MW 175.02		
6104	n-Heptyl Chloride BP 158-159°	100 g.	2.00 C
	CH ₃ (CH ₂) ₆ Cl...MW 134.65		
1331	Pyrrole BP 128-130°	500 g.	12.00 D
	NHCH:CHCH:CH...MW 67.09		
P 6123	γ-Valerolactone (Pract.) BP 73-74°/6 mm.	1 kg.	5.00 E
	CH ₃ CH(CH ₂) ₂ COO...MW 100.11		